

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 August 2001 (23.08.2001)

PCT

(10) International Publication Number
WO 01/60955 A1

(51) International Patent Classification⁷: C10L 1/06, 1/08

OX1 4TZ (GB). SCHILOWITZ, Alan, Mark [US/US];
15 N. Sixth Avenue, Highland Park, NJ 08904 (US).

(21) International Application Number: PCT/US01/09792

(22) International Filing Date: 8 February 2001 (08.02.2001)

(74) Agent: MULLER, W., G.; ExxonMobil Chemical Europe
Inc., P.O. Box 105, B-1830 Machelen (BE).

(25) Filing Language:

English

(81) Designated States (*national*): CA, JP, SG, US.

(26) Publication Language:

English

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

(30) Priority Data:

0003386.0

14 February 2000 (14.02.2000) GB

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(71) Applicant (*for all designated States except US*): EXXON-
MOBIL RESEARCH AND ENGINEERING COM-
PANY [US/US]; 1545 Route 22 East, Clinton Township,
Annandale, NJ 08801 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): PACE, Stuart
[GB/GB]; 19 Varsity Place, John Towle Close, Oxford

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*



WO 01/60955 A1

(54) Title: FUEL COMPOSITION

(57) Abstract: This invention relates to a fuel composition comprising a base fuel having a final boiling point above 150 °C and an anti-foam, characterised in that the anti-foam comprises di-isobutylene in an amount greater than 2.5 % by volume based on the total fuel composition. The addition of this anti-foam reduces the break-up time for any foam formed significantly.

FUEL COMPOSITION

5 This invention relates to fuel compositions comprising an anti-foam additive to reduce the time needed to break up any foam formation during the filling of a vehicle's fuel tank thereby enabling a more complete filling of the tank and at the same time reducing risk of spillage.

10 The problem of foaming of fuels due to entrainment of air during filling of fuel tanks of vehicles is well known. The problem has hitherto been mitigated by adding to the fuel antifoams which are substantially non-hydrocarbonaceous. An example of such a non-hydrocarbonaceous additive is a silicon containing polymer. Non-hydrocarbonaceous additives usually have to undergo a rigorous testing programme with respect to their compatibility with the fuel and also environmental considerations. However, if the additive is a hydrocarbon, especially a non-aromatic hydrocarbon, the issues of compatibility and
15 environmental considerations are not as critical. JP-A-08073870 discloses gasoline compositions for two-cycle engines which contain at least 10 vol % 7-8C olefinic hydrocarbons and have a T₅₀ of 93-105°C, a final distillation temperature of 110-150°C and an octane No. by the motor method of at least 95. Amongst the 11 olefins listed is mentioned 2,4,4-trimethyl-1-pentene. However, it is not clear whether these olefins are used
20 as a blend of several. In any event, the olefins are not used as anti-foaming agents but to achieve high output and low fuel consumption and to avoid seizure even at high compression ratios. Moreover, gasoline used in two-cycle engines (ie two-stroke engines) inevitably have lubricating oils admixed therewith and hence are not as susceptible to foaming as gasolines free of such lubricating oils.

25

Similarly, SAE Paper 950740 describes various compounds being added to a mixture of toluene (boiling point about 110°C) and isooctane (boiling point 99°C) to monitor the emissions of vehicles powered therewith. One such compound added is di-isobutylene in an amount > 15% by volume. The resultant mixture is unlikely to have a final
30 boiling point above 150°C and there is no mention of the use of di-isobutylene as an anti-foam in this document.

Similarly, JP-A-06200263 describes a composition which contains at least 65% by volume based on the total base fuel of a high boiling component with a boiling point from
35 80-120°C which uses 7-8C paraffin type or olefin type hydrocarbon. The abstract of this patent makes no mention of any other base fuels or specific olefins in this range and there is no mention of any of such olefins as anti-foaming agents.

Again WO 99/49003 discloses gasoline formulations which contain *inter alia* at least 5% volume of saturated C₇/C₈ branched chain hydrocarbons. In any event, there is no mention of the use of these as anti-foaming agents.

- 5 It is an object of the present invention to formulate a fuel compositions comprising an anti-foam which is an unsaturated, non-aromatic hydrocarbon capable of reducing the break-up time to disperse such any foams formed.

- 10 Accordingly, the present invention is a fuel composition comprising a base fuel having a final boiling point greater than 150°C and an anti-foam, characterised in that the anti-foam comprising di-isobutylene in an amount greater than 2.5 % by volume based on the total fuel composition.

- 15 The base fuels may comprise mixtures of saturated, olefinic and aromatic hydrocarbons and these can be derived from straight run streams, thermally or catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions, catalytically reformed hydrocarbons, or synthetically produced hydrocarbon mixtures. The present invention is particularly applicable to a broad range of petroleum fuels from the light boiling gasoline (which typically boils between 50 and 200°C) to distillate fuel (which typically boils
20 between 150 and 400°C). The most common distillate fuels suitable for use in the present invention as base fuels are selected from motor gasoline, kerosene and diesel fuels. The sulphur content of the base fuel is suitably less than 100 ppm by weight, is preferably less than 50 ppm by weight and more preferably less than 30 ppm by weight. Such low sulphur levels can be achieved in a number of ways. For instance, this may be achieved by well
25 known methods such as eg, catalytic hydrodesulphurisation.

- Di-isobutylene used as an anti-foam in the fuel compositions of the present invention is present in said composition in an amount greater than 2.5% by volume, suitably from 2.5% to 35% by volume, preferably 5.0 % to less than 15% by volume and is more
30 preferably present in an amount from 7.5 to less than 15% by volume of the total fuel composition. Di-isobutylene can readily be obtained by dimerisation of isobutylene. It is generally prepared from a crude mixture of olefins and usually comprises a mixture of various C₈-olefin isomers but always comprises 2,4,4-trimethylpent-1-ene admixed with 2,4,4-trimethylpente-2-ene. These two isomers are suitably present in the di-isobutylene in a
35 weight ratio of about 75% (-1-ene) to about 25 % (-2-ene).

Di-isobutylene has an advantage over other non-hydrocarbonaceous anti-foams such as silicon based polymers in that di-isobutylene is substantially miscible with conventional

fuels in all proportions. Di-isobutylene has the further advantage that current plants making methyl tert-butyl ether (hereafter "MTBE") from isobutylene and methanol (MTBE having more recently fallen out of favour upon environmental considerations), can be readily switched to convert the same isobutylene feedstock to di-isobutylene. Furthermore, di-isobutylene can readily make up the additional component volume to replace the MTBE used hitherto in automotive fuel component pool.

It has also been found that the reduction in break-up time for foams formed is not due to a dilution effect of di-isobutylene. Test results show that addition of up to 2.5% by volume of di-isobutylene in the fuel did not show any reduction in the foam break-up time of the fuel tested.

The present invention is further illustrated with reference to the following Examples:

Tests were carried out in which di-isobutylene (a mixture of 3 parts 2,4,4-trimethylpent-1-ene and 1 part 2,4,4-trimethylpent-2-ene) was added to varying quantities to a distillate fuel which was susceptible to foam formation. The resultant admixture was tested in the BNPe Anti-Foam test (French Standard Test NF M 07-075) and the results obtained are shown in Table 1 below:

TABLE 1

Blend	Fuel (ml)	DIB (ml)	DIB (%)	Foam Vol (ml)		Mean Value	Break-up Time (seconds)		Mean Value
1	300	0	0	126	124	125	79.2	82.5	80.9
2	292.5	7.5	2.5	130	128	129	79.7	81	80.4
3	285	15	5	130	132	131	62.3	66.9	64.6
4	270	30	10	142	140	141	51.9	49.6	50.8

DIB - Di-isobutylene (a mixture of 3 parts 2,4,4-trimethylpent-1-ene and 1 part 2,4,4-trimethylpent-2-ene)

Claims:

1. A fuel composition comprising a base fuel having a final boiling point greater than 150°C and an anti-foam, characterised in that the anti-foam comprises di-isobutylene in an amount greater than 2.5 % by volume based on the total fuel composition.
5
2. A composition according to Claim 1 wherein the base fuels comprises mixtures of saturated, olefinic and aromatic hydrocarbons derivable from straight run streams, thermally or catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions, catalytically reformed hydrocarbons, or synthetically produced hydrocarbon mixtures.
10
3. A composition according to Claim 1 or 2 wherein the base fuel is a petroleum fuels having a boiling range from gasoline (which typically boils in the range from 50 and 200°C with a final boiling point > 150°C) to distillate fuel (which typically boils between 150 and 400°C).
15
4. A composition according to any one of the preceding Claims wherein the base fuel is a common distillate fuel selected from motor gasoline, kerosene and diesel fuels.
20
5. A composition according to any one of the preceding Claims wherein the base fuel has a sulphur content of less than 100 ppm by weight.
6. A composition according to any one of the preceding Claims wherein the base fuel has a sulphur content of less than 50 ppm by weight.
25
7. A composition according to any one of the preceding Claims wherein the di-isobutylene comprises a mixture of 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene.
30
8. A composition according to any one of the preceding Claims wherein the di-isobutylene comprises a mixture of 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene in a ratio of 75% to 25% by weight.
- 35 9. A composition according to any one of the preceding Claims wherein di-isobutylene is used in an amount from 2.5 - 35 % by volume.

10. A composition according to any one of the preceding Claims wherein di-isobutylene is used in an amount from 5 to less than 15% by volume of the total fuel composition.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/09792

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/06 C10L1/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 199621 Derwent Publications Ltd., London, GB; Class E17, AN 1996-205833 XP002171159 & JP 08 073870 A (TONEN CORP), 19 March 1996 (1996-03-19) cited in the application abstract</p> <p>-----</p>	1-4,7-10

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

4 July 2001

Date of mailing of the international search report

17/07/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

De Herdt, O

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/09792

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 8073870 A	19-03-1996	NONE	